the double sulphate and selenate of the zinc group. This group may be safely taken as a type of the eight groups of the whole double salt series, as the thallium salts belonging to it are the two best crystallising thallium salts of the series, and so far the only ones which have been obtained in adequately perfect crystals for trustworthy investigation.

A Critical Study of Spectral Series. Part I.—*The Alkalies,*
H and He.

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(Abstract.)

It is generally recognised that one of the most hopeful means of gaining an insight into the structure of the atom is a study of the spectra of the elements, and at present especially of the series spectra. Before, however, this is possible it is necessary to have a more definite knowledge of the relationships between the various series of the same element, and corresponding series in different elements. With this end in view, the author began some years ago a systematic discussion of the data accumulated, using for this purpose the estimated errors of observation given by Kayser and Runge in their extensive and very accurate observations on these spectra. These possible errors give limits of possible variation for the different constants involved, and permit of safe conclusions being drawn. The present communication gives the results affecting the spectra of the alkalies, hydrogen and helium.

The chief results arrived at are the following :—

1. The wave numbers of any one series can practically all be represented within observational errors by a formula based on a modification of Rydberg's form, viz. :—

$$n = A - \frac{N}{(m + \mu + \alpha/m)^2}.$$

2. Calling the values of $N/(m+\mu+\alpha/m)^2$ for the integral values of m a sequence, it is shown that four sequences exist :—

(*a*) The fundamental, or F-sequence, where the denominator is $m+1-2W$, or $m+1-2W(1-m^{-1})$, where $2W$ is a small fraction of the square of the atomic weight. If w denote the atomic weight divided by 100, $2W$ is

$0.0141w^2$ for Na, and, roughly, $\frac{s}{s-1} \times 0.0141w^2$ for K, Rb, Cs, where s has the values given below. Their accurate values can be determined from the doublet separations, but the exact dependence on the atomic weight is yet to be discovered. The series depending on it are chiefly far up in the ultra-red, and the inexactness of the observations does not enable us to distinguish between the forms given above.

(b) The P-sequence, giving rise to the typical principal series. It is formed by adding a definite expression $\mu + \alpha m^{-1}$ to the corresponding term of $F(2) \times (1 - m^{-1})$. In other words, it is $1 - W(1 - m^{-1}) + (\mu + \alpha m^{-1})$. From this point of view, P may stand for positive.

(c) The D-sequence, giving rise to the typical diffuse series. It is formed by subtracting the same $\mu + \alpha m^{-1}$ from the $F(2)$, but the term in m^{-1} is not exactly determined owing to the inexactness of observations of these series. From this point of view, D may stand for difference.

(d) The S-sequence, giving rise to the sharp series. Evidence is given to show that this sequence is determined by the addition of a small constant to N, and the deduction of a number which, for the alkalies, is rather less than 0.5 from the P-sequence. The sequences are represented by writing a V before the distinguishing letter.

3. The value of the expression $\mu + \alpha m^{-1}$, of the previous paragraph, is given by $s \times 0.074560 \left(1 - \dfrac{0.21521}{m}\right)$, the numbers being correct to the last two digits in each case; s is an integer which has the values 2, 4, 5, 6, respectively for Na, K, Rb, Cs.

4. The typical series are then given by

$$VS(1) - VP(m) \quad \ldots\ldots\ldots\ldots \quad \text{Principal.}$$
$$VP(1) - VS(m) \quad \ldots\ldots\ldots\ldots \quad \text{Sharp.}$$
$$VP(1) - VD(m) \quad \ldots\ldots\ldots\ldots \quad \text{Diffuse.}$$

The principal series is given quite definitely, and all within limits of error from the relations given above. The same is the case for the diffuse so far as the μ is concerned, but the sharp is not so definite. The fundamental series is

$$VD(2) - VF(m).$$

Where doublets occur, they are formed by deducting the 2 W of the F-sequence from the P-sequence for the ordinary doublet series, or from the D-sequence for the satellite series.

5. As we pass down the alkalies from Cs to Li, there is a gradual change of type. Cs shows definite satellites in the D-series, but Rb and the others appear to possess none. The D-series of Na is not of the D-type, but of the F-type, *i.e.* $P(1) - F(m)$; traces of the normal type are, however, possibly

existent in a set of three faint diffuse lines. In Li the whole type is altered from a positive type of doublets to a negative type of singlets. The three series for Li are respectively :—

$$VS(1) - VD(m)$$
$$VD(1) - VS(\dot{m})$$
$$VD(1) - VF(m)$$

and there is apparently a remnant of the normal type (in which $s = 1$) VP (1)—VD (m) in the doublet 26,890, 26,875 ($\nu = 2\cdot10$) observed by Paschen in the ultra-red.

6. The helium series consist of the following :—

Singlet series, positive type ......$\begin{cases} VS'(1) - VP(m). \\ VP(1) - VS'(m). \\ VP(1) - VFm. \end{cases}$

Doublet series, negative type ...$\begin{cases} VS''(1) - VD(m). \\ VD(1) - VS''(m). \\ VD(1) - VFm. \end{cases}$

7. The helium spectra have been treated by the method of least squares, in order to obtain a more accurate knowledge of the value of N. It results that N has the value 109,675 of Rydberg for the series D', D'', P'', using D and P to denote those hitherto considered to be the diffuse and principal. That the value of N for the two sharp series is somewhat greater, in accordance with the evidence derived from the study of the alkalies, whilst that for P' is 109,814. The only other singlet series considered, viz. that of Li, shows indications also of a similar change in N.

8. The remarkable relation between the alkali constants as depending on the integers 1, 2, 4, 5, 6, is shown also in their atomic volumes. The densities of the alkalies at corresponding temperatures are not known accurately, at least for Rb and Cs. But taking the values given in Landolt and Börnstein's tables, there result the following values for the atomic volumes :—

$$Li \ldots\ldots\ldots \quad 11\cdot81 \ = 1 \times 11\cdot81$$
$$Na \ldots\ldots\ldots \quad 23\cdot606 = 2 \times 11\cdot80$$
$$K \ \ldots\ldots\ldots \quad 44\cdot617 = 4 \times 11\cdot15$$
$$Rb \ldots\ldots\ldots \quad 56\cdot05 \ = 5 \times 11\cdot21$$
$$Cs \ldots\ldots\ldots \quad 70\cdot584 = 6 \times 11\cdot76$$

There are thus two corroborating indications of the dependence of the alkalies, on these integers, which raise curiosity as to the nature of the missing element whose integer should be 3. It is suggested that the integers s appear in the series formulæ because the latter are really determined by the atomic volumes of the respective elements.